Ni-Cu/MgAlOx catalysts for ethanol dehydrogenation

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The low-cost ethanol availability permits to study the obtaining of different chemicals such as ethylene, ethyl ether, acetaldehyde and ethyl acetate starting from ethanol as raw material. It is important to point out that acetaldehyde can be used as a base for the production of acetic acid, acetic anhydride, ethyl acetate, butyl aldehyde, croton aldehyde, pyridine, peracetic acid, vinylacetate and many other products. It has been reported that the nature of support and promoters, the preparation method and metal content influence the activity of copper-based catalysts. The surface acidity of support was found to be responsible for side reactions like dehydration during the dehydrogenation of alcohols, which lowered the selectivity of the carbonyl product. The copper nanoparticles supported on basic carriers such as MgO and its mixed oxides, e.g. Cr_2O_3/MgO, were reported to be highly active for catalytic transformation of alcohols (dehydrogenation, lactonization of diols, coupled dehydrogenation–hydrogenation, transfer dehydrogenation, etc.) due to the synergistic effect between the basicity of support and the fast hydrogen spillover of Cu nanoparticles. In opposite to pure MgO, involving strong basic sites of O^{2-} ions, the MgO-Al_2O_3 mixed oxides, formed by the thermal decomposition of hydrotalcite (HT), $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, in addition to the strong basic sites (O^{2-}), contains surface sites of low (OH^- groups) and medium (Mg–O pairs) basicity.

Ni-Cu catalysts supported on mixed Mg-Al oxides, derivative of thermally treated HT, are the objects of the present study. The aim of the investigation is to elucidate the impact of Cu loading on the catalyst performances in the ethanol dehydrogenation reaction. The precursors were prepared by co-precipitation of a mixed Ni-(Cu)-Mg-Al nitrate solution with a Na_2CO_3 solution at the same pH and temperature, continuous stirring, constant nickel content (1.0 wt.%) and varying copper content (0.0, 5.0 and 10.0 wt.%) at the same molar ratio of Mg/Al = 5/1. The precursors were dried at 105 ^oC, followed by thermally treatment at 600 °C for 2 h. The phase composition and reducibility of the obtained mixed oxides were studied by *in situ* XRD and H_2-TPR. Prior to the reaction, *in situ* reduction with hydrogen (50 Nl/h) was performed at 500 °C for 1 h. The ethanol dehydrogenation was carried out in an automated flow catalytic unit at 260 °C, total pressure of 0.5 MPa, nitrogen/ethanol ratio of 20 and catalyst loading of 1.5 10^{-3} kg. The kinetic runs were performed by changing the ethanol space time (mass of catalyst divided by the flow rate of the feed) from 7.3 to 27 kg_{cat} s mol^{-1}.

It was found that all catalysts deactivate after 100 h run under the same conditions. The conversion of the most active 1Ni10Cu/$MgAlO_x$ catalyst drops from 40% to 13%. For all studied catalysts, the acetaldehyde selectivity of about 95% stayed unchanged depending on the space time and Cu loading.

It may be concluded that the lower space time slightly favored the methane formation. A higher Cu loading gives rise to higher acetaldehyde selectivity of 98–99%.